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DEVELOPMENT OF A PERMSELECTIVE MEMBRANE SYSTEM FOR CONTINUOUS CARBON DIOXIDE CONTROL

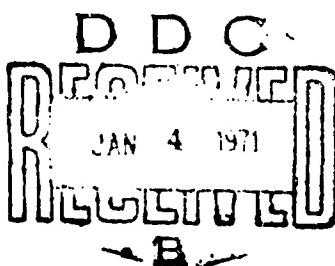
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OCTOBER 1970

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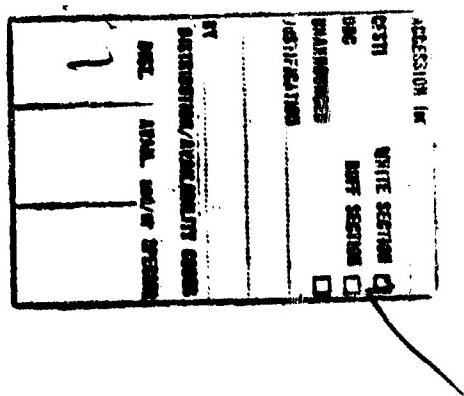
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13. ABSTRACT An immobilized liquid film of an aqueous bicarbonate/carbonate solution, and including a catalyst for the hydrolysis of CO ₂ , has been incorporated into a system for removal of CO ₂ from a life-supporting environment in space. A method of packaging the membrane is described. A one-man system, requiring 18.3 square yards of membrane, was constructed and tested. Approximately the same membrane area is required for both spacecraft cabin control and for astronaut extra-vehicular back-pack application. Permeation results are given for a variety of conditions. Virtually no oxygen is lost through the membrane, and the anticipated system has the advantage of not requiring regeneration or replacement of any components.		

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SUMMARY

This report describes the characterization and development of a membrane and membrane system capable of selectively removing CO₂ from a life-supporting environment in space. The active ingredient of the membrane, an aqueous cesium bicarbonate/carbonate salt solution, was shown by Dr. W. J. Ward (under a previous Air Force contract) to combine a high CO₂ permeability with an extremely high CO₂/O₂ separation factor. Ward also showed the feasibility of increasing both the CO₂ flux and the separation factor by addition to the solution of a small amount of sodium arsenite, a material known to catalyze the hydrolysis of CO₂. The goals of the current contract were to develop a means of immobilizing the membrane liquid, develop a procedure to incorporate such a membrane into a useful, efficient package, and to construct and test a membrane system capable of transporting CO₂ at a one-man metabolic rate.

A means of immobilizing the membrane liquid and a membrane packaging technique were developed in a separate program for the Flight Dynamics Laboratory of the Air Force, and were modified as necessary to meet the goals of the current contract. The aqueous salt solution is contained within the pores of a micro-porous, hydrophobic filter membrane (with 1% to 2% polyethylene glycol added to the solution as a surfactant). The membranes are separated from each other by polyester monofilament screens, and the manifolding procedure isolates opposite sides of the membrane from bulk gas intermixing. Each of two gas streams is divided into multiple parallel streams upon flowing through the unit.

Permeation tests were made on both single-layer and multilayer modules under a variety of conditions. Single-layer permeabilities at room temperature for the catalyzed CsHCO₃/NaAsO₂ membrane were between 325 and 375×10^{-9} cc(STP) cm thick/sec, cm², cm Hg ΔP, whereas tests on multilayer modules at the same conditions gave permeabilities of ≈ 250 to 280×10^{-9} . This lower result is attributed to poor gas distribution across the parallel flow paths in the multilayer units.

A system capable of removing 50 g/hr of CO₂ (a one-man metabolic rate) was constructed and tested. It required 18.3 square yards of membrane. The same size should be sufficient for both in-board cabin and extra-vehicular back-pack operation (at the same metabolic rate). The system's study showed that water vapor (at an absolute pressure equivalent to the vapor pressure of the aqueous membrane solution) could be efficiently used to sweep the permeating CO₂ from the membrane package. Power consumption is relatively low since only a small mass of water is required to provide the necessary sweep vapor. The vapor can then be condensed and the liquid recycled. However, imperfections in the membrane filter medium resulted in cross-membrane leaks in all but one of the modules tested when 1 atm of pressure was applied across

the membrane. Thus a full-size, water-vapor swept system could not be demonstrated. A single successful test on a 10-layer module did show the feasibility of this mode of operation.

A highly permeable and selective membrane system for removing CO₂ from a life-supporting environment has been demonstrated. However, a reliable membrane capable of supporting a large pressure difference is required for optimal performance. In addition, safeguards against possible contamination of the recycled breathing stream with arsenic-containing dusts will be a necessity for actual operation. Based on work currently in progress, it is thought that these problems can be solved.

FOREWORD

The research and development described in this report was performed under Contract No. F33615-68-C-1234, "Permselective Membrane System Development," by the Research and Development Center, General Electric Company, in Schenectady, N. Y. This work was performed between 1 January 1968 and 1 April 1970.

The program monitor for this contract is Mr. C. M. Meyer, Altitude Protection Branch, Environmental Medicine Division, Aerospace Medical Research Laboratories, Wright-Patterson Air Force Base, Ohio 45433.

The authors wish to acknowledge the valuable assistance of the following General Electric personnel: W. J. Ward, III and P. H. Kydd for their sage advice and recommendations during the course of this project, and K. Hemingway and P. Dederick for their aid in constructing and testing of the membrane system.

This technical report has been reviewed and is approved.

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TABLE OF CONTENTS

<u>Section</u>		<u>Page</u>
I.	INTRODUCTION-----	1
II.	INITIAL PACKAGING CONCEPT-----	3
III.	FINAL PACKAGING CONCEPT-----	6
	IMMOBILIZED LIQUID FILM-----	6
	PACKAGING TECHNIQUE -----	7
IV.	SYSTEM CONFIGURATION -----	10
V.	TEST RESULTS-----	17
	PRELIMINARY MEMBRANE PERFORMANCE-----	17
	FINAL SIZE MEMBRANE PERFORMANCE-----	17
	FINAL SYSTEM TESTS-----	21
VI.	CONCLUSIONS-----	23
	REFERENCES-----	24

LIST OF ILLUSTRATIONS

<u>Figure</u>		<u>Page</u>
1	Three-Layer Membrane Construction -----	3
2	Cast Membrane Package Stacking Arrangement-----	4
3	Cast Membrane Package Counter-Flow Configuration-----	4
4	Exploded View of Spacecraft Module (Final Design) -----	8
5	Special Tools Used During Module Construction: (a) O-ring cutter; (b) Hollow, razor-edged cutter; (c) Centering drill; (d) Plexiglas port-hole cutter-----	9
6	Cabin Gas Circulation Rate vs Raffinate CO ₂ Concentration ---	11
7	Vapor Sweep System Schematic-----	13
8	Atmospheric Pressure Test System--Pictorial -----	15
9	Atmospheric Pressure Test System--Schematic -----	15
10	Deliverable Test Assembly: (a) Front view; (b) Rear view ---	16
11	Cross-Flow Manifold Design -----	18
12	Membrane Scored by Coarse Screen -----	19
13	Modified Cross-Flow Manifold Design -----	20

LIST OF TABLES

<u>Table</u>		<u>Page</u>
I	Membrane Requirements for Cabin Control-----	12
II	Membrane Requirements for Back-Pack Operation-----	13

SECTION I

INTRODUCTION

Many industrial and government laboratories are focusing attention on the problems of maintaining a life-supporting environment in a variety of vehicles operating in space, the upper atmosphere, on land, and under sea. A critical problem in this area is the development of a suitable CO₂ removal system. A number of processes exist for the removal of CO₂ from gas mixtures. Most common of these are solid absorbent and liquid scrubbing processes, although regenerative adsorption with molecular sieves is currently undergoing a great deal of development for use on long-term manned space missions.

An alternative method for gas separation involves the use of permselective membranes. Membrane separation processes in general are attractive because they are inherently simple and require no regeneration or replacement of any components. Patents on potential processes date back to 1834, but to date no commercial process to separate gases using permselective membranes exists. For CO₂/O₂ separation, the best polymeric membrane is silicone rubber, which combines a high CO₂ permeability of

$$300 \times 10^{-9} \frac{\text{cc (STP)-cm thick}^*}{\text{sec-cm}^2 - \text{cm Hg}}$$

and a relatively high CO₂/O₂ separation factor (the ratio of CO₂ permeability to O₂ permeability) of 5.5. However, for a practical CO₂ removal system, this separation factor is inadequate.

In 1964, W.L. Robb considered the use of liquids as potential membrane materials (Ref. 1). Under an initial contract with the U.S. Air Force (Aerospace Medical Research Laboratory), this idea led ultimately to the development by Dr. W.J. Ward III of a highly effective immobilized liquid membrane for CO₂/O₂ separation (Ref. 2). Two projects were then conducted to further develop this membrane and to incorporate it into an efficient and compact package. During an intensive program for the Flight Dynamics

*These units will be used throughout.

Laboratory of the U.S. Air Force, a high packing density membrane scrubber was developed for use in a closed-loop, rebreathing system for pilots of fighter aircraft (one component of the Self-Contained Aircraft Oxygen System--SCAOS). During his initial investigation, Ward had found that the flux of CO₂ through the liquid membrane would be increased by addition of a catalyst (sodium arsenite--NaAsO₂) to the liquid solution comprising the film. This catalyst was not incorporated in the SCAOS membrane system because of safety considerations.

The goal of the current research was to characterize the catalyzed liquid membrane and to construct and test a membrane package large enough to support one man under spacecraft conditions. Thus, the major objectives of this project were:

1. Obtain performance data on the NaAsO₂-catalyzed membranes.
2. Investigate the possibility of using low-pressure sweeping with water vapor as an efficient means of system operation for long-term, manned space missions.
3. Design, build, and test a one-man CO₂ scrubber.

SECTION II

INITIAL PACKAGING CONCEPT

The original attempts to package the immobilized liquid membrane for CO₂ control were started in 1968 by Dounoucos and co-workers. The immobilized liquid film was to have been made by containing a 1 to 2 mil porous Dacron mat impregnated with saturated CsHCO₃ solution between backed silicone rubber membranes (Figure 1). The Dacron mat was then to be

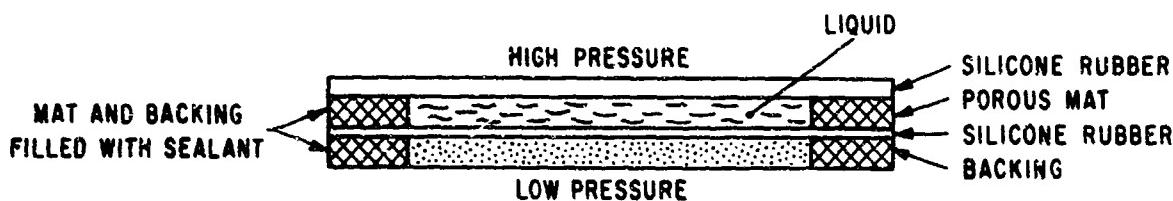


Figure 1 Three-layer membrane construction.

dried, and the package rewet by flushing with humid air before using. Before humidification, the package should thus have had identical performance to a silicone rubber package. They originally projected that a packaging density of 440 ft²/ft³ could be achieved. The proposed packaging procedure called for stacking 2 ft² membranes with a fine monofilament woven screen between each pair of membranes. Before stacking, two diagonally opposite corners of each screen were impregnated with a water-soluble wax. The screens were so stacked that the wax-impregnated corners of one screen were lined up with the unimpregnated corners of the adjacent screens. The four edges of the stack were then impregnated with a low viscosity RTV silicone rubber to a depth of 1/4 inch. A small cut was made on each corner exposing the screen edges containing wax (Figure 2). The wax was removed by a warm water wash. At this point, alternate screens at each corner were open, and the open screens of each corner were connected together in a common manifold. The CO₂-rich feed gas entered and left the package through diagonally opposite corners; the CO₂-lean sweep gas entered and left the package through the other diagonally opposite corners (Figure 3).

During the first months of this program, the basic procedures outlined above were followed. The concurrent in-house development of a silicone rubber membrane package for O₂-N₂ separation enabled modifications to be made to the above casting procedures as causes of package failures (manifold leaks, etc.) were discovered. Several 10-layer modules for CO₂-O₂ separation were constructed using various smaller, preliminary sizes of membranes. A recurring problem with the CO₂ packages involved cross-membrane leakage, which appeared to be the result of pinholes in the silicone

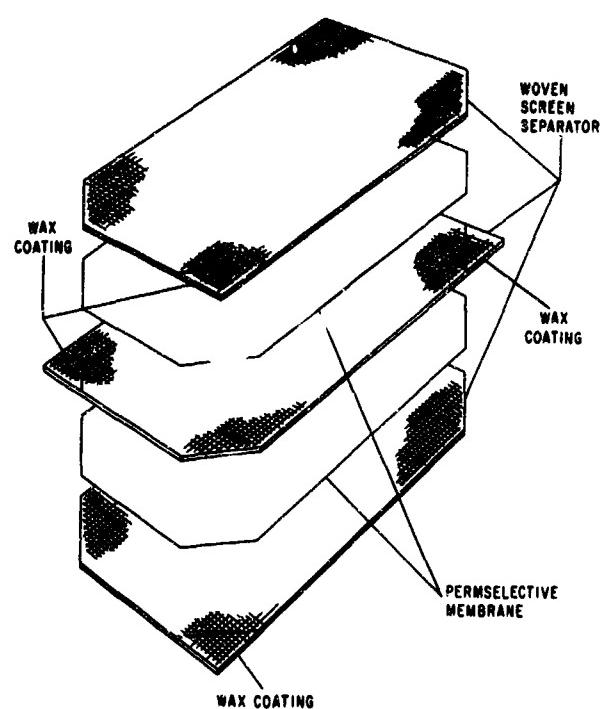


Figure 2 Cast membrane package stacking arrangement.

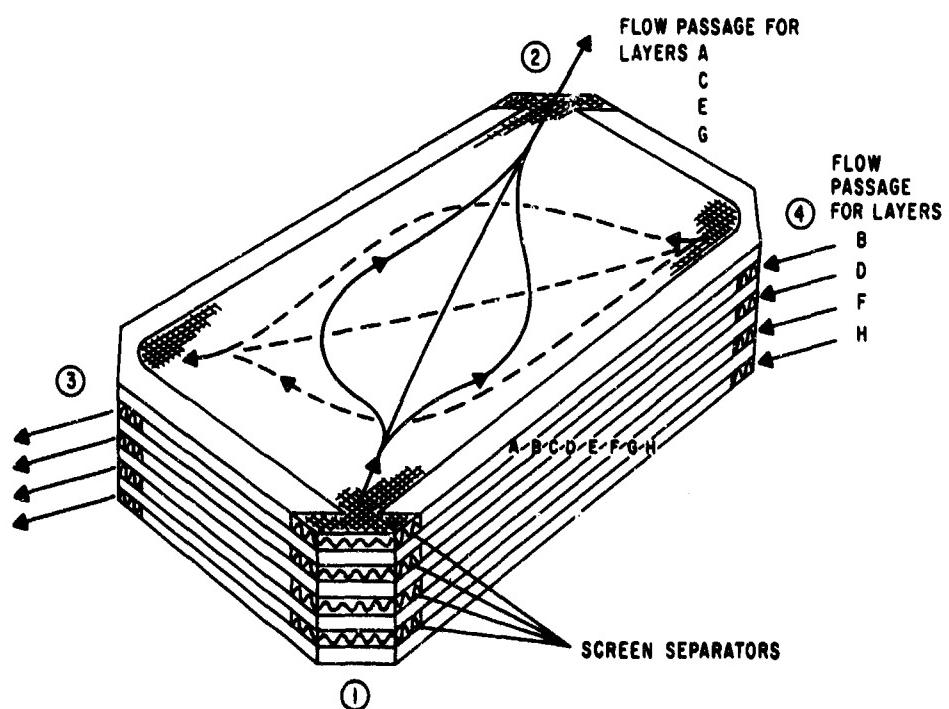


Figure 3 Cast membrane package counter-flow configuration.

rubber, and which resulted in very low CO₂/O₂ separation factors. A rigorous inspection procedure for the silicone rubber/liquid film laminates was established. Each laminate was inspected just prior to packaging. The results indicated that the laminates were clearly developing pinholes after they were made. After exploring a number of possible causes, we concluded that the caustic CsHCO₃ solution chemically attacked the silicone rubber. Several 1- by 2-foot laminates had been prepared for incorporation into a 5 square yard test package. However, with the above conclusion, work on this contract was halted pending an examination of other possible membrane materials.

SECTION III

FINAL PACKAGING CONCEPT

In December 1968, project responsibility for the spacecraft system was transferred to the Chemical Processes Branch of the General Electric Research and Development Center. With the failure of the silicone rubber laminate structure, it was realized that a new membrane, and perhaps a new fabricating technique, must be employed. An intensive program to develop a CO₂ control system as part of a closed-loop, rebreathing system (SCAOS) for the Air Force Flight Dynamics Laboratory was underway; thus, it was decided to stop work on the spacecraft system pending the results of SCAOS. Sufficient knowledge and experience were gained to resume work on the spacecraft system in August 1969.

IMMOBILIZED LIQUID FILM

Once we realized that the CsHCO₃ solution chemically attacked the silicone rubber used to enclose and support the solution-impregnated Dacron mat, a search was begun for new methods of immobilizing the liquid film. During the SCAOS investigation, a microporous, hydrophobic film manufactured under the tradename "Solvineert" by the Millipore Corporation was found to provide such a method. The Solviveert films used for SCAOS had a nominal pore size of 0.25μ, a porosity of ≈70%, and a thickness of 5.0 mils. During the present contract, we learned that Millipore was developing a new grade of Solviveert film with a somewhat tighter pore structure (≈0.20μ pores) while maintaining a porosity of 70%, as before. Millipore claimed that they had better quality control of this grade, and could produce a more uniform film, so this material was used for the final product. The Solviveert film was unaffected by the aqueous salt solutions to be used in this project to a temperature of ≈70°C. The bubble point of the liquid-impregnated film (the pressure required to blow liquid out of the pores of the film) was determined to be in excess of 30 psi. Thus, a film of Solviveert impregnated with aqueous CsHCO₃/NaAsO₂ solution could be used as the immobilized liquid membrane without any supporting or bounding material (e.g., silicone rubber sheets) for pressure differences across the membrane of approximately 15 psi or less. Since the present system was intended to demonstrate the performance of a catalyzed membrane package large enough for one man, not an optimized high-pressure ratio system, we hoped that this membrane would be adequate.

The CsHCO₃ used in all experiments was supplied as a saturated aqueous solution (~6.4 M, 99.9% pure). Sufficient NaAsO₂ was added to this solution to make the resulting mixture 0.25 M in NaAsO₂. To impregnate the somewhat hydrophobic Millipore film, a small amount of polyethylene glycol (1% to 2%, by volume) was mixed into the aqueous solution. The equilibrium vapor pressure of this solution corresponded to a relative humidity of ≈70% to 75%. The films were then immersed in solution and allowed to soak for

several hours. Upon removal from the solution, excess liquid was drained from the film surface and the films were stored between absorbent paper towels (in a humid room maintained at 70% to 75% relative humidity). The film surface was essentially free of liquid before its inclusion into a package.

Several chemistry texts (Ref. 3) state that, in basic solution, arsenite will be oxidized to arsenate, thereby losing its catalytic activity. Several solutions of sodium arsenite/cesium bicarbonate were therefore prepared and analyzed over a period of 2 weeks. Samples were stored at room temperature, elevated temperature (70 C), and with humid O₂ bubbling through the solution (at room temperature), and none showed any loss of arsenite through oxidation. Analyses were performed using a standard titration of arsenite with permanganate. Thus, it was concluded that the sodium arsenite catalyst was sufficiently stable under anticipated operating conditions to warrant its use in the liquid membrane.

PACKAGING TECHNIQUES

The basic concepts and procedures for fabricating working membrane packages were conceived and developed during the SCAOS program. Some modifications of these techniques were required for the spacecraft application.

Polyester monofilament screens were washed, pressed, and precut to size. The screens were so positioned between membranes as to channel and distribute gas over the membrane surface.

The pressure drop due to gas being forced laterally through a screen was found to be (for a given length of screen) strongly dependent on the screen thickness, screen mesh, and volumetric gas flow. As will be discussed later, it was deemed necessary for system operation to have a very low pressure drop for a high (volumetric) flow of gas on the sweep side of the package. Thus, to maximize packing density consistent with the system requirements, two different plastic screens were used:

PE 400 (manufacturer's designation)--13 mils thick, 400 μ mesh openings, 47% open area

PE 1120--24 mils thick, 1120 μ mesh openings, 58% open area.

The "feed" gas (high concentration of CO₂) would be forced across the PE 400 screen. The "sweep" gas (used to dilute and remove the permeating CO₂) would be swept across the PE 1120 screen.

A multilayer membrane module was built of alternate layers of membranes and screens (Figure 4). Adjacent screens (separated by a membrane) were themselves alternated so that one side of each membrane was in contact with a "feed" screen while the opposite side of the membrane was in contact with a "sweep" screen.

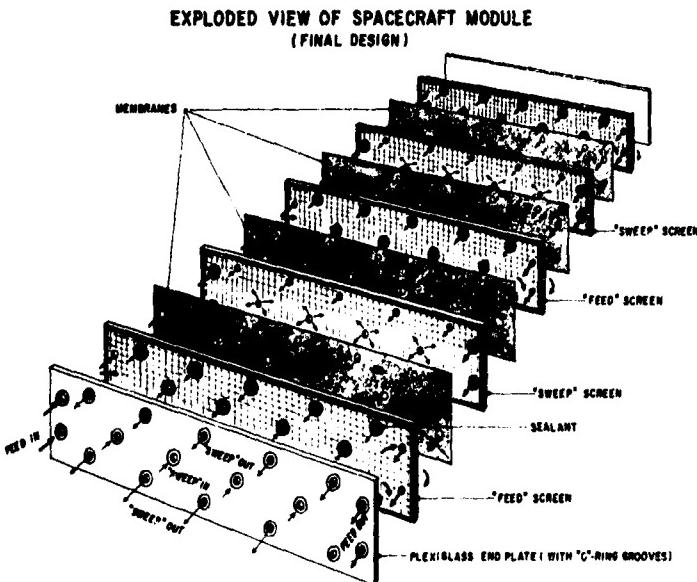


Figure 4 Exploded view of spacecraft module (final design).

A liquid epoxy resin system was used to bond the perimeter of all layers and to seal and isolate adjacent screens from each other. An air-powered sealant gun was used to apply a narrow bead of the epoxy resin about the perimeter of a screen. Additional amounts of the epoxy resin were placed at premarked manifold positions on each screen. A membrane was then laid on top of this screen, and the next screen placed on top of the membrane. The epoxy was then applied to this screen. This procedure was followed until 20 membranes had been used in the stack. A 1/16-inch-thick Plexiglas plate was used as one module end-plate. A 1/4-inch-thick Plexiglas plate with predrilled manifold holes was used as the top module end-plate. O-ring grooves were precut about each of these manifold holes with a special tool [Figure 5 (a)]. The module was then securely clamped between heavy plates and the epoxy allowed to cure. An additional amount of epoxy was then placed about each of the four edges of the module to ensure a complete edge seal.

To obtain a strong bond between the Plexiglas and the epoxy, the surface of the Plexiglas was treated with a strong acid solution (a mixture of chromic and sulfuric acids) and then flushed with water. This treatment hydrolyzed the acrylic Plexiglas surface and enabled the epoxy to bond to it. When this epoxy had cured, the module was drilled out at each of the manifold positions with a hollow, knife-edged tool [Figure 5 (b)]. The membranes and screens were cut away up to the solid 1/16-inch Plexiglas bottom end-plate. Correctly sized and positioned holes were then cut in this plate using the centering drill and cutting tool [Figure 5 (c), (d)]. These tools were designed to prevent shavings from being forced into and thereby blocking the open screens.

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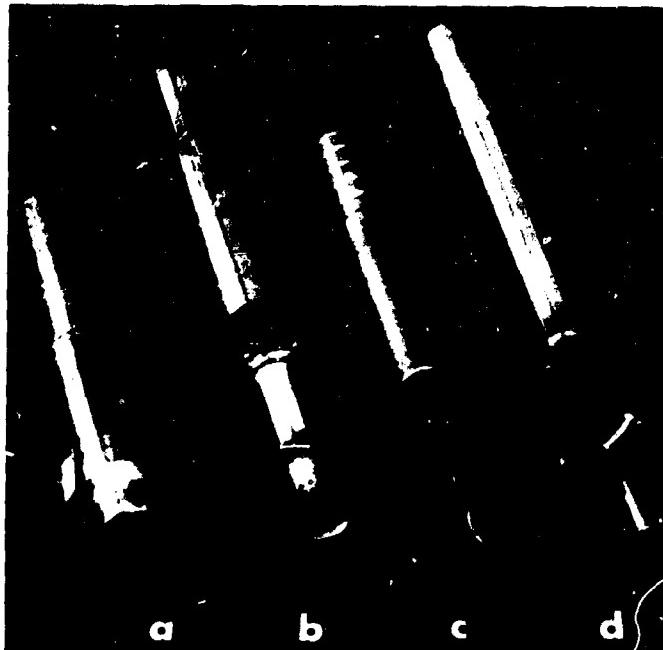


Figure 5 Special tools used during module construction; (a) O-ring cutter; (b) Hollow, razor-edged cutter; (c) Centering drill; (d) Plexiglas port-hole cutter.

The module should then have been ready to test. During testing of the final design modules several of the feed ports were found to be sealed after drilling, leading to poor gas distribution (and performance) in the module. A primary cause of this was apparently the spreading of the epoxy from the border edge into and around the manifold hole areas. This problem was overcome by inserting a small high-speed hand drill with a cylindrical file attachment into the drilled port hole and grinding away a small amount of screen and membrane material. The module end plates were not touched by the grinding tool, so the pre-cut O-ring seals could still be used.

From calculations based on a heat transfer analogy (Ref. 4), it was concluded that a cross-flow system would be essentially (>95%) as efficient as an ideal counter-flow system under the anticipated operating conditions. Since it was originally planned to operate the sweep side of the scrubber under vacuum conditions (at \approx 14 mm Hg total pressure) the sweep flow manifold configuration was designed to permit the necessary flow rate with a low-pressure drop (< 1 mm Hg). The large number of manifold ports were designed to ensure a uniform distribution of gas over each membrane.

SECTION IV

SYSTEM CONFIGURATION

The CO₂-removal system was originally planned to provide CO₂ control both for spacecraft cabin control and for astronaut extra-vehicular back-pack application. Membrane requirements for the two cases were considered under a variety of operating conditions. Essentially equal area requirements for the two cases were required for reasonable operating parameters of flow rates, operating pressures, etc; (and at the same metabolic rate).

A major goal of this contract was to operate the CO₂ scrubber with a pure water-vapor sweep. In an actual system, this would facilitate water and CO₂ recovery for reuse. Thus, the sweep side operating pressure was set by the equilibrium water-vapor pressure of the CsHCO₃/NaAsO₂ solution (70% to 75% of saturation). The CO₂ permeating through the membrane would dilute the vapor stream, and, at constant total pressure, lower the partial pressure of water vapor. Because of the drying effect this would have on the membrane, the minimum water flow was determined by the CO₂ flux and the critical range of allowable relative humidity. A total humidity change of 10% to 15% (due to dilution with CO₂ and to pressure drop through the package) was considered tolerable. Thus, for removal of 50 g/hr of CO₂, and assuming that the flow pressure drop could be made essentially negligible by proper selection of screen size and manifold design, a minimum water flow of 184 g/hr would be required (at any system operating condition). The power required to generate this water vapor would be 124 watts. It should be noted that this minimum sweep flow rate is solely determined by the CO₂ removal rate, and is independent of any feed flow conditions.

A second requirement of the current membrane system was the necessity of having less than a 20 psi pressure differential across feed to sweep (due to the Solvinert film bubble point of 30 psi). By combining the contract specifications for cabin atmosphere (maintainence of a CO₂ partial pressure of 7.6 mm Hg at 258 mm Hg total cabin pressure), a reasonable design basis for cabin atmospheric control was to compress the cabin gas to 760 mm Hg total pressure, thereby increasing the CO₂ partial pressure to 22.4 mm Hg. Small, lightweight compressors capable of handling the flows and compression ratio required for the above configuration were found to be currently available or could be designed for such aerospace applications.

The cabin gas circulation rate is determined by the raffinate (feed exit) CO₂ concentration (for fixed CO₂ inlet concentration and removal rate). These data were plotted in Figure 6. Since a constant CO₂ partial pressure (~33 mm Hg) is exhaled regardless of total system pressure, the above membrane package and system should also be within design limits for back-pack operation.

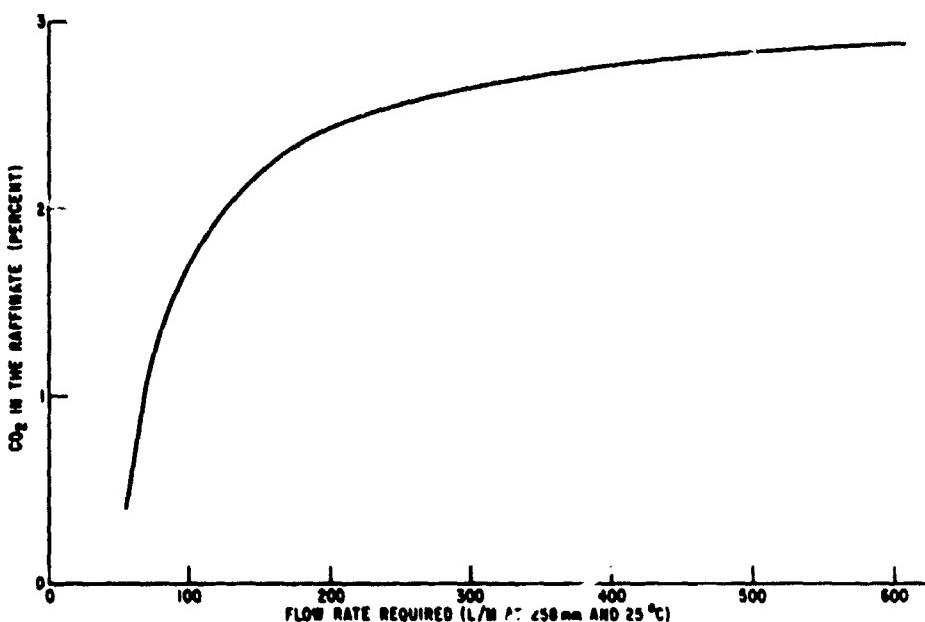


Figure 6 Cabin gas circulation rate vs raffinate CO₂ concentration.

Small cross-membrane leaks, assumed to be a result of pinholes in the Solvinert films, were found in each of the final modules, thereby making it impossible to operate the modules with a large pressure difference across the membranes. Since the amount of leakage was negligible if no pressure difference was applied across the membrane, a system was also designed for operating the membrane package with both feed and sweep sides at atmospheric pressure. Humid air was then used as the "sweep" gas. These conditions were proposed solely for test purposes, and would not be those used in actual spacecraft operation.

Table I lists the membrane requirements for several feed and sweep flows for the cabin control system (based on a CO₂ inlet partial pressure of 22.8 mm Hg and a CO₂ removal rate of 50 g/hr). Table II presents the same data for face mask operation, using a breathing rate of 13 liters/min, a CO₂ inlet partial pressure of 33 mm Hg, and a CO₂ removal rate of 50 g/hr. A CO₂ permeability of 350×10^{-9} was used to obtain the area calculations (membrane area is inversely proportional to permeability, for extrapolation to other permeabilities.) From these numbers both system possibilities might be handled with about 19 to 20 square yards of active membrane.

The test system designed for vacuum water-vapor sweeping is shown schematically in Figure 7. The water-vapor generator was maintained at a temperature 4 or 5 C below room temperature. The water vapor was warmed to room temperature as it passed through the coil of copper tubing and thence into the sweep side of the membrane package (which was at room temperature). Hence, the water-vapor pressure was about 70% of saturation

TABLE I
Membrane Requirements for Cabin Control

- Assumptions
- 1) $Pr_{CO_2} = 350 \times 10^{-9}$
 - 2) Feed and Sweep at 760 mm Hg
 - 3) Partial Pressure CO₂ in Feed = 22.8 mm Hg
 - 4) CO₂ Removal Rate = 50 g/hr

<u>Feed Flow (liters/min)</u>	<u>Sweep Flow (liters/min)</u>	<u>Membrane Area (sq yd)</u>
15	30	63.1
15	45	52.7
15	60	49.0
15	75	47.0
30	60	21.0
30	90	19.8
30	120	19.3
30	150	19.2
45	90	17.7
45	135	17.0
45	180	16.8
45	225	16.6

TABLE II
Membrane Requirements for Back-Pack Operation

- Assumptions
- 1) $Pr_{CO_2} = 350 \times 10^{-9}$
 - 2) Feed and Sweep at 760 mm Hg
 - 3) Partial pressure CO₂ in feed = 33 mm Hg
 - 4) Breathing rate = 13 liters/min
 - 5) CO₂ removal rate = 50 g/hr

<u>Feed Flow (liters/min)</u>	<u>Sweep Flow (liters/min)</u>	<u>Membrane Area (sq yd)</u>
13	26	18.4
13	39	16.6
13	52	15.8
13	65	15.4

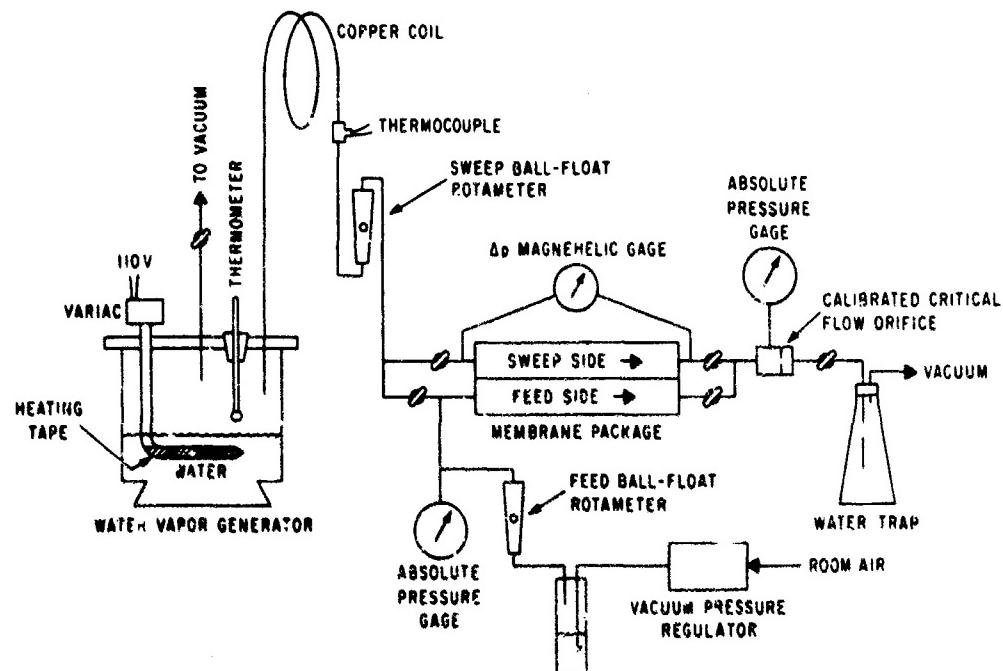


Figure 7 Vapor sweep system schematic.

on the sweep side. The size of the calibrated critical-flow orifice was chosen to yield the desired water-vapor flow rate.

Water-saturated air was supplied to the feed side of the membrane at a regulated pressure. The flow of humid air to the membrane package was measured through a small rotometer.

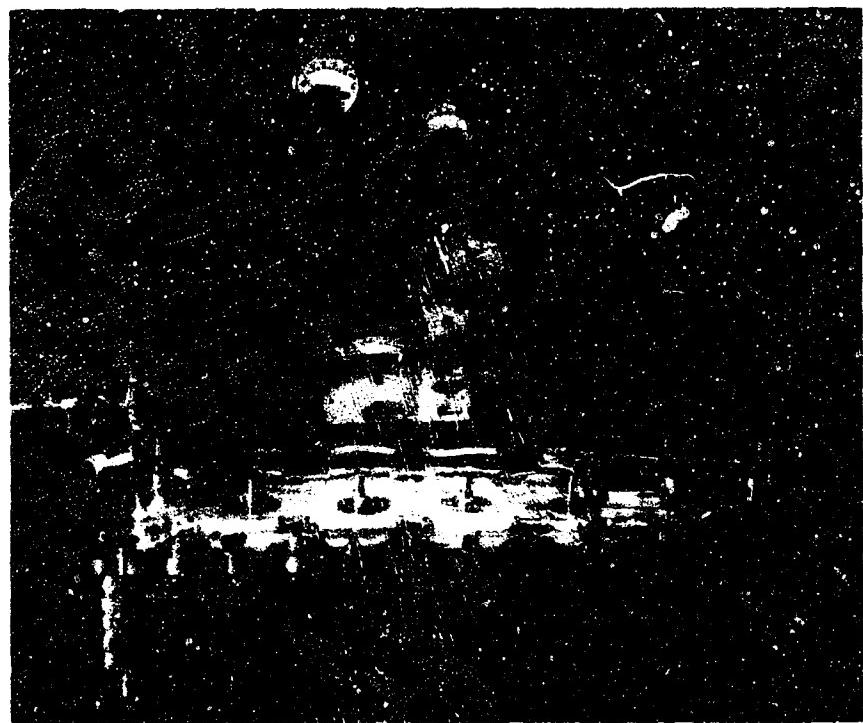
Pressures on the two sides of the membrane were controlled independently. Except for transient feed flows observed when the feed-side pressure (vacuum) regulator was adjusted, there should have been no steady flow of gas into the feed side when it was isolated from the low-pressure sweep side of the system. A steady flow was an indication of leakage through a membrane from feed to sweep sides.

The test procedure for this system was as follows:

1. With the vacuum regulator closed (i.e., set for zero pressure on the vacuum side), a steady flow of water vapor was established through both the sweep and feed sides. The pressure upstream of the critical flow orifice was generally held around 15 mm Hg.
2. Stopcocks at the inlet and exit feed ports were closed, thereby isolating the feed side from the sweep.
3. The vacuum pressure regulator was adjusted to give the desired pressure on the feed side. This adjustment caused a surge of humid air (measured by the ball-float rotameter) into the feed side; however, the flow then decreased to zero in the absence of leakage from the feed to the sweep.
4. After steady conditions were established, the pressure drop of the sweep flow from inlet to outlet ports was measured on the Magnehelic differential pressure gauge.
5. The feed pressure was raised in steps of about 100 mm Hg to 1 atm absolute or until leakage from feed to sweep occurred. The sweep ΔP was observed at each step of the feed pressurization.

The test system shown in Figure 8 and schematically in Figure 9 was assembled for the atmospheric sweep testing. Flows were regulated by calibrated critical flow orifices. Both gas streams were humidified by blending a water-saturated and dry gas stream before entering the package. Differential and absolute pressure gauges were placed in the system to monitor pressure conditions during operation.

The deliverable test assembly was fundamentally the same as above, but constructed in a more compact unit. It is shown in Figure 10.



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Figure 8 Atmospheric pressure test system--pictorial.

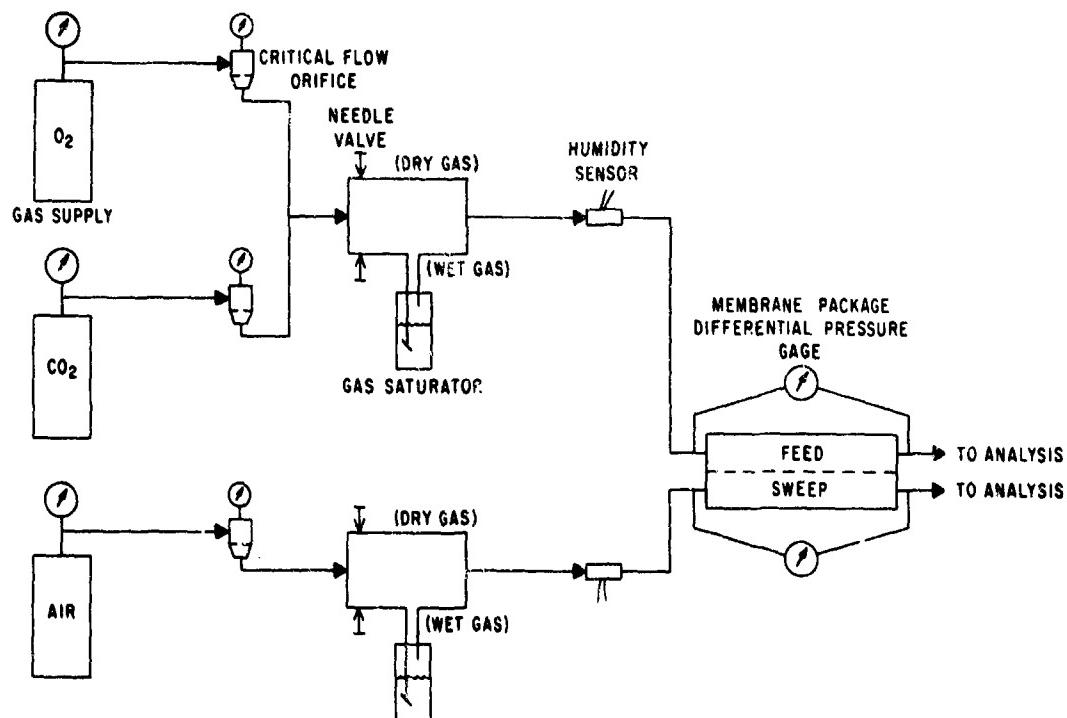
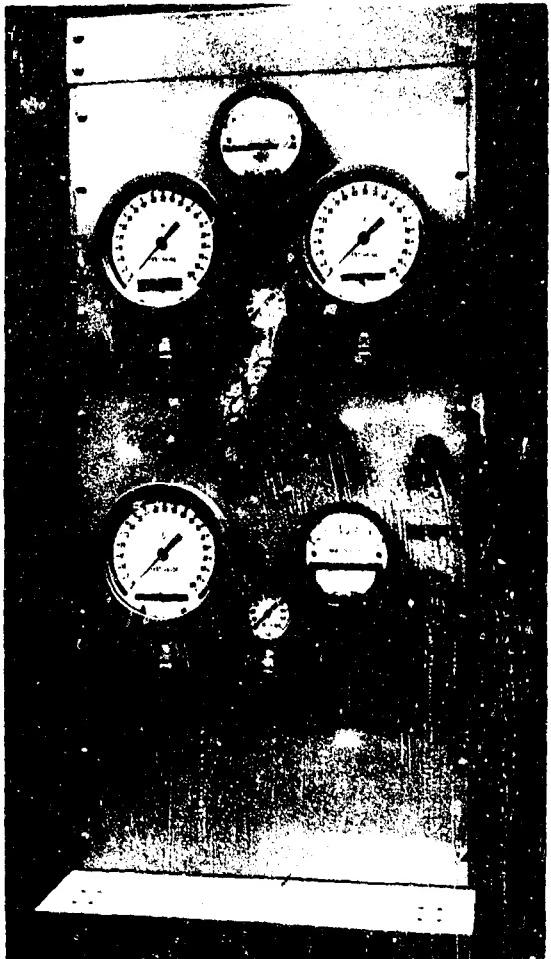
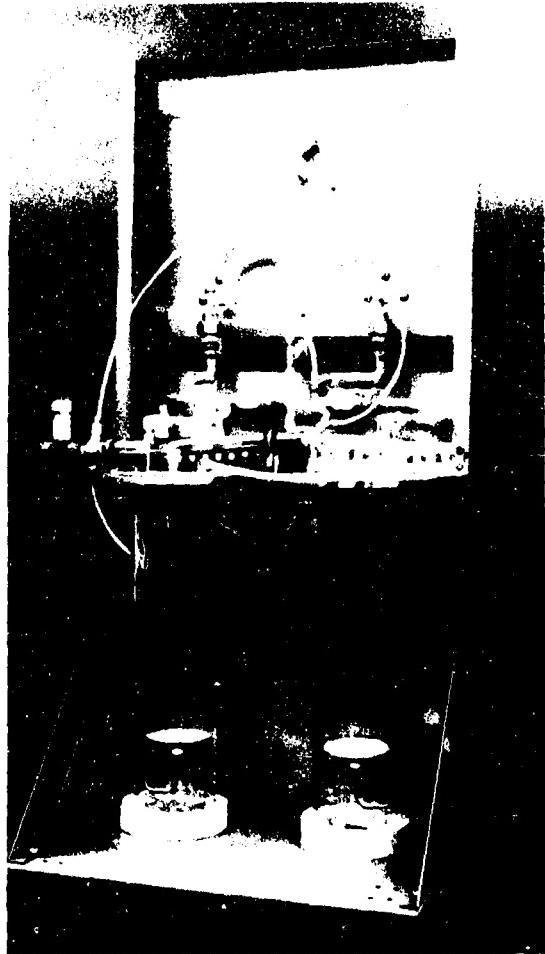


Figure 9 Atmospheric pressure test system--schematic.



(a)



(b)

Figure 10 Deliverable test assembly: (a) front view; (b) rear view.

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SECTION V

TEST RESULTS

PRELIMINARY MEMBRANE PERFORMANCE

Initial performance data were obtained from a series of tests on single-layer membrane modules. Using a 12- by 13 1/4-inch membrane, in a diagonal flow configuration (the same size membrane and flow configuration as used for SCAOS), a series of runs was made (at atmospheric pressure) to determine the effect of flow rate, CO₂ concentration, and temperature on the CO₂ permeability of the membrane.

There appeared to be no effect on the calculated permeability of this membrane due to sweep flow rate. However, the permeability did appear to increase as the feed flow rate is increased. The permeability rose from 386×10^{-9} to 473×10^{-9} as the feed flow rate was increased from 0.78 to 2.0 cc/sec/feed screen. These values were obtained for an inlet concentration of 4.9% CO₂ at 25 C. In actual operation, a spacecraft membrane system would see higher gas flows than those above, so the higher permeability might be expected. A possible explanation for this effect was that the gas was more evenly distributed over the entire membrane area at the higher flow rates.

There appeared to be no effect of CO₂ concentration on the calculated permeability of the catalyzed membrane. Room-temperature data were obtained for inlet CO₂ concentrations of 3.0%, 4.9%, and 5.2%; the permeability of each run was calculated to be about 430×10^{-9} . More data should be obtained for the 3.0% run, however, since the accuracy of the gas sampling device at these conditions was insufficient. The calculated permeability for this case is only within 10% to 15%.

At the higher feed flow rates, there appears to be no effect of temperature on this membrane's permeability. Measurements at the same flow rates and inlet CO₂ concentrations each had a permeability of 430×10^{-9} at both 25 and 35 C. Since future tests were all to be run at room temperature, the lack of a temperature effect was not explored further. (Recent studies have shown, however, that there is an increase in permeability with temperature, but that the effect is much smaller than with an uncatalyzed membrane.)

FINAL SIZE MEMBRANE PERFORMANCE

A single-layer module using a 12-inch by 26-inch membrane was constructed. A cross-flow manifold design was used (shown schematically in Figure 11). We calculated that, at the CO₂ concentrations to be encountered in this study, this flow configuration was essentially as efficient (>95%) as an

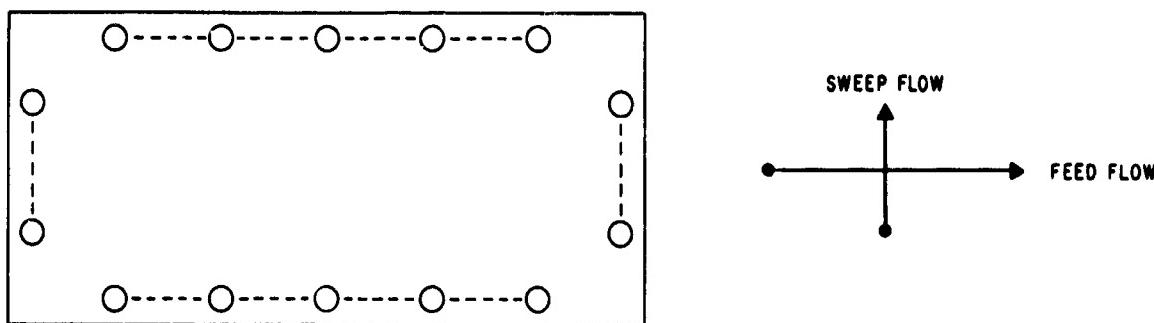


Figure 11 Cross-flow manifold design.

ideal counter-flow design. At atmospheric pressure, this module had a CO_2 permeability of 350×10^{-9} , which compared favorably with the results obtained on the smaller membrane module.

This module was then connected to the vacuum-water vapor generator equipment. Both feed and sweep sides of the module were evacuated. A vacuum-tight seal proved that there were no edge leaks or plumbing leaks on the system. With the feed exit port closed, the feed pressure was slowly increased while maintaining a small water vapor flow over the sweep side of the membrane. We quickly observed that a pressure difference of more than 100 to 200 mm Hg could not be applied to the module before a cross-membrane leak would develop. This leak started as a small flow of gas from the high-pressure feed side to the low-pressure sweep side, but which rapidly increased. The exact location of leakage was determined since a dry area was observed on the membrane about the point of leakage.

One method of rewetting, and perhaps resealing pinhole leaks, was tried. The module was flooded with $\text{CsHCO}_3/\text{NaAsO}_2$ solution, the excess of which was then drained off. This technique succeeded in rewetting the module (no leaks were found under small pressure differences), but again, as the pressure was increased to 100 to 200 mm Hg, the same type of leakage was observed. This procedure was repeated several times, and two areas of leakage were found. The module was taken apart and the membrane was examined. The membrane itself was severely scored by the screen, and there were many areas which, by visual observation, appeared to be punctured (Figure 12). However, upon closer examination under a microscope, it was found that these points actually had a thin skin of film over them. Several samples were tested for bubble point and in each case but one, the sample still had a bubble point of over 30 psi. The one exceptional case was a piece that included the area of leakage. Thus, the inability to operate this module under a pressure difference was not conclusively proved to be due either to an initially faulty membrane or to a pinhole caused by the screen indentation.



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Figure 12 Membrane scored by coarse screen. 20X

A second module was constructed incorporating ten of the above-sized membranes and with the same manifold configuration. At 21.5 C, this module had a permeability of 260×10^{-9} . In previous SCAOS tests, multi-layer module permeabilities were found to be $\approx 25\%$ to 35% lower than single-membrane permeabilities. Thus, the above results showed the same percentage lowering of permeability. This lower permeability had been, and still is, attributed to a poor distribution of gas flow among the many parallel paths through the package. However, this permeability was still 3 to 4 times greater than the previous results for uncatalyzed membranes at equivalent conditions.

This module was then connected to the vacuum-water vapor generator apparatus. Again both feed and sweep sides of the module were evacuated. A sweep flow rate of 45 cc/sec (at 16 mm Hg pressure at the sweep exit) was maintained. The feed side (exit ports closed) was pressurized fully to 1 atm with no leakage nor membrane breakthrough. The sweep side pressure drop at this flow rate was 1 mm Hg. The sweep flow and pressure drop were successfully maintained at these conditions for 2.5 hours. The system was then shut down. The critical flow orifice was replaced to enable the greater sweep flow rate which would be required under anticipated operating conditions (≈ 50 cc/sec/sweep screen). The feed and sweep sides were again evacuated and a sweep flow rate of ≈ 190 cc/sec was established. The feed side was again successfully pressurized to 1 atm without any resulting cross-membrane leakage. At this flow rate, the sweep flow pressure drop was 5.5 mm Hg. Thus, at a sweep inlet pressure of 18 mm Hg, the exit pressure was 12.5 mm Hg. The module was successfully run at these conditions for 1 hour. However, since the equilibrium partial pressure of water at the membrane package temperature of 23 C is ≈ 15 mm Hg, it would not be

possible to maintain these conditions indefinitely without drying the membranes. Also, during actual operation, the permeating CO₂ would dilute the vapor stream and lower the water vapor partial pressure even further. Thus, this module was not used for an actual permeation run. The achievement of this test was the proof that a module could withstand a pressure difference of 1 atm without leakage and that there was no apparent damage to the membranes due to the screen embossing. Also, the water-vapor generator equipment was used successfully for the first time.

A modified manifold design was utilized in another 10-membrane module (module 7) to lower the sweep pressure drop and thus enable continuous operation. This design is shown schematically in Figure 13 and pictorially in Figure 4. By enabling the sweep gas stream to divide, and thus

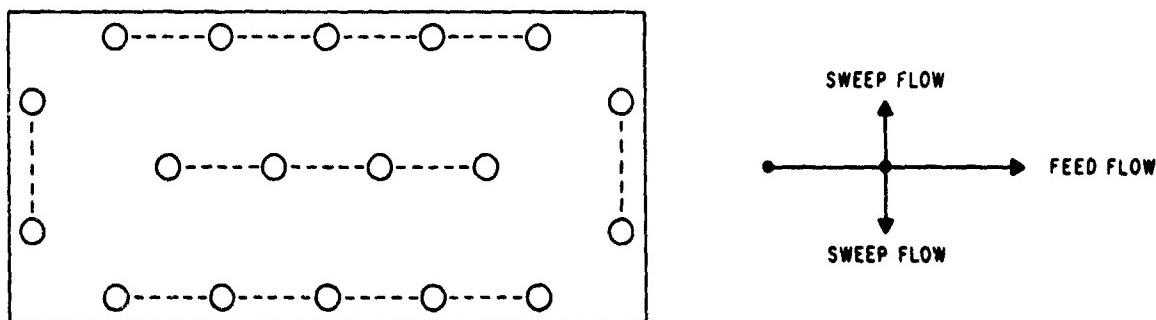


Figure 13 Modified cross-flow manifold design.

having half of the gas flow over half of the screen, it was anticipated that this modified manifold design would lower the sweep pressure drop by a factor of 4. This module was tested under vacuum conditions. A cross-membrane leak developed as the feed side was being pressurized, and drying was observed on one of the outside visible membranes. The module was rewet by pressurizing the dead-ended feed side with 100% humid air at a pressure \approx 10 mm Hg higher than the sweep pressure. The dry spot on the membrane slowly disappeared and the cross-membrane flow fell to zero. After this initial drying, the feed side was successfully pressurized to 1 atm. The sweep pressure drop was reduced by about a factor of 3; this was sufficient to begin actual permeation tests.

The module was run with feed gas containing CO₂ at a partial pressure of 22 mm Hg and at a flow rate of \approx 1/10 the flow for a one-man system. The sweep water vapor flow rate was 205 cc/sec. The system was operated for 75 minutes, at which time the CO₂ partial pressure in the raffinate was 8.5 mm Hg. Based on the feed inlet and outlet concentrations, the CO₂ permeability of this module was calculated to be 380×10^{-9} . This test

marked the first time that a module was run successfully at rated flows with the water-vapor sweep. The system was then shutdown for the night.

Attempts to reproduce this result the next day failed when we found that the module would no longer withstand an atmosphere pressure difference without leaking. The module was rewet several times, and could withstand small pressure differences, but it would not take the full load. The reason for this failure was investigated, but without success.

Six additional modules (modules 8 through 13), each containing 20 membranes and using the final design flow configuration, were constructed. Each of these modules had a small cross-membrane leak with 1.5 psi differential pressure across the membrane. Thus, it was not possible to operate these modules with a water-vapor sweep. Modules 7, 8, 9, and 10 were combined (for a total package of 70 membranes) for testing. With feed and sweep flow rates of \approx 130 and \approx 536 cc/sec, respectively, and a feed inlet CO₂ partial pressure of 34.7 mm Hg, the permeability of this package was calculated to be \approx 160 \times 10⁻⁹. This value was much lower than expected and was attributed to a grossly unequal flow distribution in the package. Each module was then individually tested for pressure drop. We found that module 9 had a feed pressure drop of 1.85 psi at a flow of 36 cc/sec, whereas modules 8 and 10 had pressure drops of only 0.47 and 0.64 psi, respectively, at this flow. This would essentially bypass module 9 from useful work. Subsequently, the final three modules were tested in the same way and were found to have similarly high feed pressure drops (1.5 to 2.5 psi) at the above flow. The sweep pressure drops for all of the modules were the same.

Module 11 (which also had a high cross-membrane leak rate) was dissected to determine the cause of the high feed pressure drop. We saw that the epoxy border seal encircled the feed port holes on several of the feed screens, thereby preventing flow through those screens and raising the pressure drop through the module. Modules 9, 12, and 13 were repaired by grinding away a small amount of the membranes and screens within the feed ports with a small, high-speed power drill. Care was taken not to disturb either of the Plexiglas module end-plates. The pressure drops (at the test flow above) were reduced for each of the repaired modules to 0.33 to 0.43 psi. Two of the modules (after repair) had a relatively high cross-membrane leak (\sim 5 cc/sec at 1.5 psi differential pressure), but with both sides of the membrane package at atmospheric pressure, and with very low pressure drops in the system, this leak-rate was tolerable.

FINAL SYSTEM TESTS

Modules 7 through 10, 12, and 13 (a total of 110 membranes) were stacked between Plexiglas manifold plates and were tested for the final system. Feed flows were designed for a 1-man flow system. For an inlet flow of \approx 13 liter/min, and an initial CO₂ partial pressure of 39.5 mm Hg (a calibration error made this concentration higher than the 33 mm Hg desired), the

CO_2 permeability of the entire system was calculated to be $\approx 260 \times 10^{-9}$. The CO_2 partial pressure in the feed stream was reduced from 39 to ≈ 12 mm Hg.

As a final test on the complete system, direct breathing into the membrane package was accomplished. A two-hose face mask was used, with pure O_2 being supplied through the inhale line and the exhaled breath being supplied directly to the membrane scrubber through the exhale line. Direct breathing was maintained for only 40 minutes, as the feed side pressure drop was too high for comfortable exhalation (maximum ΔP of 0.4 psi). At the end of this time, the CO_2 pressure in the exhaled breath was reduced from 33.4 to 5.3 mm Hg. Although direct breathing was not maintained for a sufficient time to ensure steady-state operation, scrubbing under actual breathing conditions was demonstrated. The data were in accord with test observations on the SCAOS.

SECTION VI

CONCLUSIONS

The immobilized liquid film originally developed by Ward for the continuous removal of carbon dioxide has now been incorporated into two working systems. The first application (SCAOS) used an uncatalyzed membrane because of safety considerations. For the current spacecraft application, sodium arsenite was added to the aqueous CsHCO_3 solution to catalyze the hydrolysis of CO_2 and increase the membrane's efficiency.

A membrane package capable of removing 50 g/hr of CO_2 was constructed and tested. The unit contained 110 membranes, each 1 by 2 feet, incorporated within six modules. The membrane package had a CO_2 permeability of

$$260 \times 10^{-9} \frac{\text{cc (STP)-cm thick}}{\text{sec-cm}^2 - \text{cm Hg}}$$

with both sides operating at atmospheric pressure. This result is ≈ 4 times greater than that of an uncatalyzed membrane package at equivalent conditions.

For actual spacecraft operation, it would be desirable to operate the sweep side of the package with a water-vapor sweep stream (at a total pressure equal to the equilibrium vapor pressure of the aqueous solution). This would enable recovery and reuse of both components of the $\text{CO}_2\text{-H}_2\text{O}$ sweep stream, a necessity for long-term missions. A single test on a 10-layer module under these conditions showed a CO_2 permeability of 360×10^{-9} . Thus, the feasibility of this mode of operation was demonstrated.

Because no effort was expended under the present contract to develop a membrane specifically for the spacecraft application which could operate with a high pressure difference across it, most of the modules constructed had small cross-membrane leaks under an applied pressure difference. Thus, they could not be tested under the desired system conditions. The cause of this type of failure is not definitely known, although we believe the leaks are a result of pinholes or weak spots in the Solvinert film.

Since a bare membrane was used for this system, with direct contact of the breathing gas with the arsenite-containing film, it could not be used safely in a closed-loop system because of possible contamination of the feed gas with arsenic-containing dusts. The next stage of development for this system would substitute a composite film for the current bare one. We believe that this would prevent any arsenic-containing dusts from contaminating either gas stream, and that it would enable a higher pressure difference to be applied across the membrane. Other means of immobilizing the liquid membrane should also be considered.

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